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NAVY DEPARTMENT  
OFFICE OF NAVAL RESEARCH  
WASHINGTON, D. C.

12 July 1954  
Report No. 840  
(Quarterly)  
Copy No. 6



# INVESTIGATION OF LIQUID ROCKET PROPELLANTS



Contract N7onr-462

Task Order No. III

Project No. NR 220 023

**Aerojet-General** CORPORATION

A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY  
AZUSA, CALIFORNIA

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By direction of  
Chief of Naval Research (Code 429)

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12 July 1954

Report No. 840  
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Task Order III  
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AEROJET-GENERAL CORPORATION

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CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order III, and covers the work done from 1 March through 31 May 1954.

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I. SUMMARY

A. Evidence for the formation of formaldoxime in the initial step of the thermal decomposition of nitromethane is presented.

B. N-chloroethylenimine, a potentially valuable intermediate in the synthesis of hydrazine derivatives containing the three-membered ethylenimine ring, was prepared for the first time by the reaction of ethylenimine and sodium hypochlorite.

C. In a few attempts to produce N-aminoethylenimine by the action of liquid ammonia on chloroethylenimine, a 15% yield, based on reducing-function analysis, was obtained.

D. No tetramethylammonium acetylide was isolated from the decarboxylation of tetramethylammonium propiolate, or from the action of acetylene on tetramethylammonium triphenylmethide.

II. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

## A. INTRODUCTION

The study of the thermal decomposition of nitromethane at pressures of approximately 250 psia was continued. The principal aims of this investigation are to ascertain the mechanism of the decomposition and to determine the importance of a chemical delay time in nitromethane rocket motors.

## B. EXPERIMENTAL RESULTS

1. Several mass-spectrometer product analyses for the decomposition of nitromethane with and without additives were reported previously (References 1,2). Two requirements should be met in order to have confidence in these analyses: (1) duplicate analyses must yield reproducible data, and (2) the ratio of carbon to nitrogen among the products must be 1:1,\* as in nitromethane. Table I shows three product analyses from decomposition tests of nitromethane alone at 355°C and after 5 min duration. The reproducibility of the data is satisfactory, and since the experimental conditions are such that only relatively minor improvements in precision could be made, the time involved in performing additional tests would not be warranted. For decomposition tests with nitromethane alone, approximately 1:1 carbon-to-nitrogen ratios were obtained. The product analyses from tests with additives, however, showed the following inconsistencies, which are especially pronounced with added oxygen:

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\* Hydrogen and oxygen are less reliable as a means of checking the mass balance, since the quantitative determination of water by means of a mass spectrometer is not as reproducible as that of most other compounds.

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a. The carbon-to-nitrogen ratios were usually greater than one.

b. The total nitrogen content of the products was not always reproducible.

c. The distribution of nitrogen and its oxides showed considerable variation.

2. In order to determine the cause for the high carbon-to-nitrogen ratio, a comparison was made between the per cent nitromethane decomposed as determined by polarographic analyses (Reference 3) and the per cent decomposed as derived from total carbon or total nitrogen of the products, determined by mass spectrometer analyses. It is shown in Table II that for the tests with nitromethane alone these comparisons agree very well. In the runs with added oxygen the per cent decomposed, based on carbon, is noticeably higher than that determined by the polarographic analyses, whereas the percentages based on nitrogen agree more closely with the latter. It appears, therefore, that in the tests with added oxygen, the total carbon content of the products may be too high, but that the nitrogen content may be close to the actual value. It is believed that the high carbon-to-nitrogen ratio is brought about by the interaction between the source filament in the mass spectrometer and nitrogen dioxide, which is one of the products of the decomposition of nitromethane in the presence of oxygen. The problem of the mass-spectrometer analysis of nitrogen dioxide was studied extensively by Friedel and co-workers (Reference 4) and at Aerojet-General (Reference 5). It was found that nitrogen dioxide reacts with carbon deposited on the source filament to form carbon dioxide and carbon monoxide, thereby increasing the carbon-to-nitrogen ratio. The results of these investigations suggested that the mass spectrometer source must be conditioned with nitrogen dioxide prior to analysis. Although such a procedure was followed in the present investigation, it appears that a more extensive conditioning may be required than has heretofore been used.

3. The non-reproducibility of total nitrogen content of the products may also be related to the interaction of nitrogen dioxide or other oxidizing agents with the mass-spectrometer source. Friedel and co-workers reported that compounds other than nitrogen dioxide are not affected by the conditioning procedure, and this appeared to have been borne out by previous work at Aerojet-General. However, it has been shown during the present investigation that the cracking pattern of nitromethane can be altered considerably by conditioning with oxidizing agents. Although nitromethane itself is not determined mass spectrometrically, this has a bearing on the analyses of other compounds, since many of the mass peaks overlap.

4. The following reasons for the inconsistencies in the distribution of nitrogen and its oxides may be advanced:

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a. Nitrogen dioxide may react with carbon to form nitric oxide or nitrogen, depending on whether carbon monoxide or carbon dioxide is the other product.

b. Reactions among nitrogen oxides may occur in the interval between the termination of the decomposition test and the actual analysis.

c. In some cases, air had apparently entered the system during the analysis. Although corrections for air can be made, it may cause a change in the distribution of the nitrogen oxides because of interactions with oxygen.

5. Inconsistencies similar to those observed for oxygen were encountered also with added ethylene oxide and chromium acetylacetonate (Reference 2). It is difficult to decide whether nitrogen dioxide is responsible for them, since there is no visual evidence for its presence, as is the case with added oxygen; or whether another compound acts similarly to nitrogen dioxide. A third possibility is that materials analyzed in the mass spectrometer prior to these samples are responsible for the inconsistent results.

6. In view of the difficulties encountered with these analyses, known mixtures consisting of nitromethane, nitric oxide, nitrogen dioxide, nitrous oxide, and oxygen will be prepared and analyzed in the mass spectrometer under varying conditions. It is believed that a more thorough knowledge of the behavior of these mixtures will be of considerable help in clarifying the inconsistencies observed.

7. Formaldoxime was prepared by the method of Scholl (Reference 6) and a mass spectrum of this compound was obtained. Since formaldoxime is a possible product of the thermal decomposition of nitromethane its spectrum was compared to the product spectra from nitromethane decomposition tests, but no evidence for its presence among the products could be detected. One decomposition test was carried out with nitromethane and 2.5% formaldoxime. The products from this test were analyzed mass spectrometrically and a substantial increase in hydrogen cyanide was noted.

### C. DISCUSSION

#### 1. Chemical Delay Time

In all tests with added oxygen, it was found that the amounts of hydrogen cyanide as well as the organic cyanides in the decomposition products are greatly diminished. In previous reports the hypothesis had been presented that oxygen brings about sustained combustion in nitromethane rocket motors by the removal of intermediate compounds such as the cyanides (Reference 2). By this action, the chemical delay time, which is represented by the time required to transform the intermediate products to

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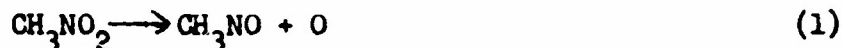
## II Kinetic Study of the Thermal Decomposition of Nitromethane, C (cont.)

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final products, is substantially decreased. It is believed that although a number of uncertainties have yet to be clarified, the data obtained during this report period still support this hypothesis.

### 2. Mechanism of the Decomposition

a. The following is a consideration of the initial step in the thermal decomposition of nitromethane. Taylor and Vesselovsky (Reference 7) proposed that the initial reaction occurs as follows:



Cottrell, Graham, and Reid (Reference 8), however, maintain that the initial step is:



and state that reaction (1) is unlikely on energetic grounds for the following reasons: the heat of formation of nitromethane is known to be -12.2 kcal/mole and that for atomic oxygen +59.1 kcal, and the heat of formation of nitrosomethane is estimated to be in excess of +2 kcal on the basis of several assumptions, the validity of which is very uncertain and will be discussed below. These values for the heats of formation result in a heat of reaction for (1) of at least 73 kcal. On the other hand, the heat necessary to bring about reaction (2) is shown to be 52.3 kcal. Because the observed activation energy is 53.6 kcal and no appreciable chain reaction appears to be occurring Cottrell and co-workers conclude that reaction (2) is more likely than reaction (1).

b. In arriving at a heat of formation of +2 kcal for nitrosomethane, Cottrell, Graham, and Reid make the following assumptions:

(1) The heat of formation of nitrosomethane ( $\text{CH}_3\text{NO}$ ) is greater than that for formaldoxime ( $\text{CH}_2\text{NOH}$ ), to which it isomerizes.

(2) The heat of isomerization of acetamide ( $\text{CH}_3\text{CONH}_2$ ) to acetaldoxime ( $\text{CH}_3\text{CHNOH}$ ) is the same as the heat of isomerization of formamide ( $\text{HCONH}_2$ ) to formaldoxime ( $\text{CH}_2\text{NOH}$ ). If this is granted and if the heats of formation for acetamide, acetaldoxime, and formamide are known, the heat of formation for formaldoxime can be computed.

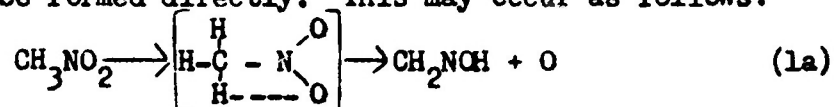
(3) Trouton's rule is sufficiently accurate to estimate the heats of vaporization for acetamide, acetaldoxime, and formamide. This assumption has to be made, since the heats of formation for these compounds are known only in their solid states.

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c. It will be shown in the following discussion that these assumptions are very unreliable, and that no definite conclusions concerning the likelihood of reaction (1) or (2) should be based on them. The first assumption stated in the previous section is probably correct; however, it may not be necessary to assume the formation of nitrosomethane, since formaldoxime may be formed directly. This may occur as follows:



The activation energy for reaction (1a) would then represent the energy necessary for forming the transition complex, which in turn will stabilize itself by the simultaneous elimination of an oxygen atom and the formation of formaldoxime. In regard to the second assumption, it is by no means certain that the two isomerization reactions have identical heats of reaction. In the case of acetamide, for instance, there is a probability for resonance between the carbon-oxygen double bond and the hyperconjugated form of the methyl group ( $\text{H}_3\text{C}-$ ), which may lower the energy by as much as 5 kcal. With formamide, hyperconjugation cannot occur, which results in a lower heat of isomerization for formamide. This, in turn, would yield a lower positive heat of formation for formaldoxime or make it negative. With reference to the third assumption, it is known that highly polar compounds, such as formamide and acetamide, do not obey Trouton's rule. In the case of formamide, an additional uncertainty is introduced, because this compound does not have a well-defined boiling point, but decomposes at 210.7°C. For these reasons, the value of +2 kcal for the heat of formation of formaldoxime may be in error by 10 or more kcal and as a consequence, the heat required for reaction (1) may be considerably lower than 73 kcal.

d. On the basis of the considerations in the previous section, reaction (1) or (1a) cannot be eliminated solely on the theoretical evidence presented by Cottrell; but this does not prove that reaction (1) or (1a) is actually the first step in the decomposition of nitromethane. There is experimental evidence, however, which indicates very strongly that reaction (1) or (1a) may be important. C. S. Coe and T. F. Doumani (Reference 9) report that if nitrosomethane is subjected to prolonged heating above its melting point at 122°C, it is converted to formaldoxime. It may be assumed, therefore, that above 350°C, nitrosomethane is very rapidly converted to formaldoxime, and irrespective of whether reaction (1) or (1a) occurs, only the formation of formaldoxime and oxygen atoms need be considered. If the rate of decomposition of formaldoxime were relatively slow, a test for its presence among the decomposition products should give a clear-cut answer to the question of whether reaction (1) is of importance in the decomposition of nitromethane. H. A. Taylor and H. Bender (Reference 10) studied the decomposition of formaldoxime at 350 to 415°C. They determined a first-order rate constant,  $k = 109.5 e^{39,000/RT} \text{ sec}^{-1}$ , for the reaction, but they also found that the decomposition is markedly accelerated by very small amounts of nitric oxide and that the primary products are hydrogen



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cyanide and water. The rate constant for the decomposition of pure formaldoxime is approximately equal to that for nitromethane,\* but the concentration of nitromethane would be considerably larger than that of formaldoxime and the latter should therefore be detectable. However, since nitric oxide, which is a major product of the decomposition of nitromethane, increases markedly the rate of decomposition of formaldoxime, its detectability in small amounts is very doubtful. A confirmation of this was obtained when a mixture of nitromethane and 2.5 mol % formaldoxime (approximately the amount of formaldoxime that might be expected to form during the decomposition of nitromethane) was allowed to decompose for five minutes at 355°C, and no formaldoxime could be detected (Section B-7).

e. Since it is known from the work of Taylor and Bender that hydrogen cyanide and water are the principal products of the pyrolysis of formaldoxime, this fact may be used to gain information on the importance of reaction (1) in the thermal decomposition of nitromethane. The absence of hydrogen cyanide would prove definitely that reaction (1) does not occur; however, its presence could be taken only as an indication that reaction (1) may be important, unless there is additional evidence that formaldoxime is the actual source of the hydrogen cyanide. An examination of the experimental results shows that Cottrell, who studied the decomposition at subatmospheric nitromethane pressures, could not obtain a positive test for hydrogen cyanide, although a faint odor of hydrogen cyanide was detected occasionally. During an investigation at Aerojet-General, which was also conducted at subatmospheric nitromethane pressures (Reference 11), one mass-spectrometer analysis of the products showed that approximately 15% of the nitromethane that had reacted formed hydrogen cyanide and 27% formed methane. In the present investigation, which is carried out at nitromethane pressures of approximately 15 atmospheres, even larger amounts of hydrogen cyanide are found, but smaller amounts of methane. After 5 minutes at 355°C, 0.38 mole of hydrogen cyanide and 0.10 mole of methane were formed per mole of nitromethane decomposed. It was also shown that even after two minutes (Reference 1) similarly large percentages of hydrogen cyanide are produced. The fact that hydrogen cyanide is found in such large quantities and in the very early stages of the decomposition is an indication that reaction (1) may be important; however, additional evidence must be produced to show that this reaction is the most likely source for the hydrogen cyanide. In the experiment with 2.5 mol% added formaldoxime, it was found that the percentage of hydrogen cyanide had increased from 38 to 53%. It can be shown that the additional percentage of hydrogen cyanide is equivalent to the amount of hydrogen cyanide that should be formed from the added formaldoxime.

\* The rate constant for the decomposition of nitromethane at subatmospheric pressures,  $k = 10^{14.5} e^{53,600/RT}$  was used. The rate constant for the decomposition of formaldoxime under the present conditions is assumed to be equal to that for its decomposition under the conditions used in Taylor and Bender's work.

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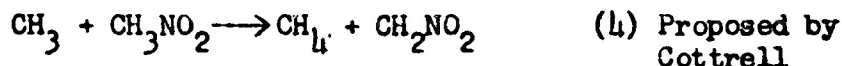
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f. Additional evidence for the occurrence of reaction (1) may be adduced by studying the relationship between the formation of hydrogen cyanide and methane. If reactions



are the only initial steps, and if the only other mechanism for the consumption of nitromethane is by reaction with the radical produced in the initial step:



then 0.5 mole hydrogen cyanide should be formed per mole of nitromethane decomposed if step (1) alone occurs, and 0.5 mole methane if step (2) is the sole initial reaction. Cottrell found that only 0.3 mole methane is formed per mole of nitromethane decomposed, and this was confirmed by the analysis carried out at Aerojet-General, wherein 0.27 mole of methane was produced. The same analysis showed that 0.15 mole hydrogen cyanide is formed per mole of nitromethane decomposed. The sum of the two fractions, 0.42 mole, is very close to 0.5 mole, indicating that perhaps both initial steps are important. In the present investigation at high pressures, it was found that 0.11 mole of methane and 0.38 mole of hydrogen cyanide are formed. The sum of the two fractions was again close to 0.5 mole, but the mole ratio of hydrogen cyanide to methane has increased from 0.55 to 3.45. This may indicate that although both initial reactions occur over the pressure range studied, reaction (2) predominates at low pressures and reaction (1) at high pressures. It is realized that the evidence presented is not conclusive, and that additional proof should be obtained, but there is considerable likelihood that reaction (1) is important in the thermal decomposition of nitromethane.

## III. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

### A. INTRODUCTION

During the present report period efforts were centered about the preparation of N-aminoethylenimine from the reaction of N-chloroethylenimine with liquid ammonia. N-chloroethylenimine, a potentially valuable intermediate in the synthesis of hydrazine derivatives containing the 3-member ethylenimine ring, was prepared for the first time from ethylenimine and aqueous sodium hypochlorite. Attempts to prepare N-chlorohydrazines from certain alkyl hydrazines and aqueous sodium hypochlorite were unsuccessful.



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## B. PREPARATION OF N-CHLOROETHYLENIMINE

1. N-chloroethylenimine was prepared as follows: A solution of 92.4 g of sodium hydroxide pellets (2.2 moles) in 385 g of water was kept at -5 to -10°C while 80.3 g of chlorine (1.1 moles) was introduced. The addition of chlorine was followed by the gain in weight of the solution. To the resulting hypochlorite solution, 43 g (1.0 mole) of cold (-10°C) ethylenimine\* was added rapidly. The reaction is exothermic and the final temperature was +10°C. The N-chloroethylenimine separated as a colorless upper layer, and the hypochlorite solution was decolorized completely. The layers were separated, and the organic layer was washed four times with 30-ml portions of distilled water to remove any unreacted ethylenimine. The yield of crude product was 90 per cent of the theoretical. Titration of the washings with 0.103N HCl, using a brom phenol blue indicator, required respectively 19.7 ml, 1.3 ml, 0.4 ml, and 0.4 ml. The product was dried over anhydrous magnesium sulfate, and distilled at reduced pressure through a 12-in. column packed with glass helices. The yield of product (bp<sub>245</sub> 37.5 to 38.3°C) was 80 per cent of the theoretical. There was no appreciable forerun or pot residue.

2. A middle cut (bp<sub>245</sub> 38.0°C) gave the following analysis:

	<u>% C</u>	<u>% N</u>	<u>% H</u>	<u>% Cl</u>	<u>Total</u>
Calculated for C <sub>2</sub> H <sub>4</sub> NCl	30.99	18.07	5.20	45.74	100.00
Found	30.98	18.09	5.13	45.72	99.92

Proof of the presence of oxidizing (positive) halogen was obtained by mixing a weighed amount of N-chloroethylenimine with ethylene chloride, adding an excess of solid potassium iodide, acidifying with glacial acetic acid, and titrating the liberated iodine with standard thiosulfate solution to the starch endpoint. The values obtained for oxidizing halogen were 100.0 per cent and 99.7 per cent, based on the formula C<sub>2</sub>H<sub>4</sub>NCl. Pure N-chloroethylenimine is a colorless, mobile, strongly lachrymatory liquid,  $n_D^{20} = 1.4433$ , immiscible with water, but miscible with ethanol and with organic solvents. It differs from other alkylchloramines, such as dimethylchloramine, in that it is appreciably more stable. Although N-chloroethylenimine appears to be stable at ambient temperatures, there is evidence for partial decomposition when it is distilled at atmospheric pressure at 70 to 71°C. A sample so distilled shows infrared absorption bands at 5.88  $\mu$  and 7.36  $\mu$ , while these bands are entirely absent in crude, dried, undistilled N-chloroethylenimine, or in material distilled at 38°C under reduced pressure. The presence of the ethylenimine ring in N-chloroethylenimine is indicated by the presence

\* The ethylenimine (bp 55 to 56°C) was obtained from Monomer-Polymer Corporation, Leominster, Massachusetts.

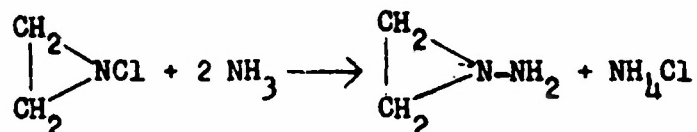
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of infrared absorption bands at 8.26  $\mu$  and at 11.7  $\mu$ ; these frequencies have been attributed to ring deformation in the spectrum of ethylenimine itself (Reference 12).

## C. REACTION OF N-CHLOROETHYLENIMINE WITH LIQUID AMMONIA

1. At the present time, only preliminary results are available on the reaction of N-chloroethylenimine with liquid ammonia to form N-aminoethylenimine:



In initial experiments, the reactants were mixed in glass ampoules at about  $-40^\circ\text{C}$ , and the mole ratio of ammonia to N-chloroethylenimine was always about 15:1. The ampoules were sealed while cold, and immediately placed in a constant-temperature bath at  $53^\circ\text{C}$ . After reaction times of 15 min to 3 hr the ampoules were removed from the bath and opened at  $-40^\circ\text{C}$ . The contents were poured into precooled Erlenmeyer flasks. The ampoules were then washed with water to remove solids (presumably ammonium chloride), and the combined washings and original reaction mixtures were acidified with 6N HCl and titrated with standard potassium iodate solution to determine the amount of reducing function present. In this connection, it was assumed that the oxidation of N-aminoethylenimine by potassium iodate involves a four-electron change (Reference 13). It was found that at  $53^\circ\text{C}$  the yield increased with the time of reaction, but that the maximum yield was only about 10%. When higher temperatures were employed, several pressure bursts of the glass ampoules occurred, and it became necessary to resort to a small stainless steel (304) reactor.

2. Several reactor designs using standard AN coupling nuts and plugs were found to be unsatisfactory, since leaks inevitably developed at the higher temperatures, especially for reaction times of 1 hr or longer. Recently, a suitable reactor (Figure 1) was designed, and runs were conducted at 73, 85, and  $98^\circ\text{C}$ . The maximum yield, obtained at  $98^\circ\text{C}$  within 15 minutes, is about 15 percent. Future work on this reaction will be concerned with a selection of suitable reaction conditions, and the isolation of N-aminoethylenimine from a large-scale (2 to 3 moles) run. One feature of the reaction, of immediate concern, is the possibility of the opening of the ethylenimine ring through the catalytic action of the ammonium chloride formed (Reference 14). The addition of the required amount of a base, such as  $\text{Ba}(\text{OH})_2$ , to the reaction mixture may prevent this ring opening by destroying the ammonium chloride as it is formed.

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## D. ATTEMPTED PREPARATION OF N-CHLOROHYDRAZINES

Attempts to prepare N-chloro derivatives of unsym.-dimethylhydrazine and trimethylhydrazine which could be used in the synthesis of methyl triazanes were unsuccessful. The experiments were carried out in the manner described above for the preparation of N-chloroethylenimine. In each case, a highly exothermic reaction (undoubtedly oxidation) occurred when the hydrazine was added to the hypochlorite solution, and no oil separated under these conditions.

IV. STUDY OF THE FEASIBILITY OF EMPLOYING ACETYLIDE SALTS AS PROPELLANT COMPONENTS

## A. INTRODUCTION

Continued efforts directed toward the preparation of tetramethylammonium acetylide by the metathetical reaction of tetramethylammonium chloride with sodium acetylide in several solvents have been unsuccessful. Tetramethylammonium propiolate was synthesized for the first time, but the preparation of tetramethylammonium acetylide by decarboxylation was unsuccessful. Elaborate precautions were taken to synthesize tetramethylammonium triphenylmethide in an atmosphere of nitrogen entirely free from carbon dioxide, oxygen, and water. No tetramethylammonium acetylide was isolated after reaction of the tetramethylammonium triphenylmethide with acetylene.

## B. METATHETICAL REACTION IN SEVERAL SOLVENTS

Previous study (Reference 3) of the metathetical reaction of tetramethylammonium chloride with sodium acetylide in liquid ammonia, pyridine, and diethyl ether indicated that solubility relationships in these solvents were not conducive to the precipitation of tetramethylammonium acetylide or sodium chloride. Investigation of this reaction was extended to the following additional solvents representing aliphatic, halogenated aliphatic, nitrogen- and oxygen-containing heterocyclic and aromatic types. The solvents used were heptane, carbon tetrachloride, pyridine, tetrahydrofuran, and benzene. Saturated solutions of tetramethylammonium chloride and sodium acetylide were prepared in each of the anhydrous solvents and mixed in an atmosphere of dry nitrogen in a dry box. No evidence of reaction was apparent after 96 hours. Because the possibility of preparing alkyl ammonium acetylides by the metathetical reaction appeared remote, attention was directed to other synthetic approaches.

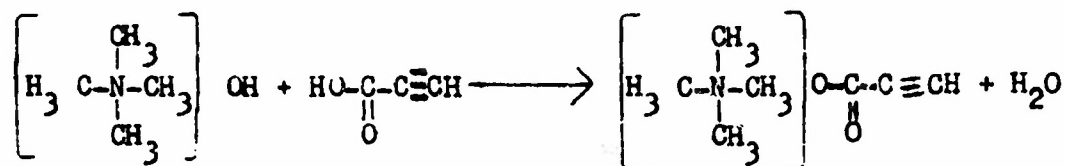
## C. PREPARATION OF TETRAMETHYLAMMONIUM PROPIOLATE

1. The decarboxylation of copper propiolate to produce copper acetylide (Reference 15) suggests that tetramethylammonium acetylide might be prepared by decarboxylation of tetramethylammonium propiolate. The synthesis of tetramethylammonium propiolate, a compound as yet unreported

## IV Study of the Feasibility of Employing Acetylide Salts as Propellant Components, C (cont.)

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in the literature, was carried out as follows:



Tetramethylammonium hydroxide was prepared by the reaction of tetramethylammonium bromide with an excess of  $\text{Ag}_2\text{O}$  in water solution. After being shaken for 3 hr at room temperature, the solution was filtered, and a portion was acidified with acetic acid and tested with silver nitrate. The absence of cloudiness indicated that the aqueous tetramethylammonium hydroxide was free of bromide ion. Propiolic acid (Farchan Chemical Corporation) was titrated with a water solution of tetramethylammonium hydroxide, using a pH meter to determine the end point. After evaporation to dryness under vacuum (12 mm) at 33 to 35°C, the salt was recrystallized twice from n-amyl alcohol, and a small portion was dried in an Abderhalden drier for 3 hr at 40°C. The melting point in a sealed capillary tube was 129°C. Analysis of a sample yielded the following:

	<u>% C</u>	<u>% H</u>	<u>% N</u>
Calculated for $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$	58.70	9.15	9.78
Found	55.78	9.19	9.28

The calculated carbon/nitrogen ratio is 7; the ratio found was 7.01.

2. The major portion of the salt was dried in a vacuum desiccator over  $\text{P}_2\text{O}_5$  for 6 days. The melting point was 134 to 135°C and remained unchanged after 5 days additional drying. The extremely hygroscopic salt was dried further before analysis and was found to contain 57.28% carbon, 8.72% hydrogen, and 9.62% nitrogen, thus yielding a carbon to nitrogen ratio of 6.95.

3. Further characterization of the compound showed that it was soluble in ethyl alcohol, soluble in boiling pyridine, slightly soluble in n-butanol, insoluble in ether, pyridine, carbon tetrachloride, and tetralin. The presence of acetylenic function is demonstrated by the formation of a precipitate when ammoniacal silver nitrate is added to an aqueous solution of the compound. Vigorous reaction and decoloration were observed when bromine in carbon tetrachloride was added to the solid salt. The presence of the tetramethylammonium ion was confirmed by the preparation of the picrate, mp 312°C (lit 312 to 313°C).

4. The infrared spectrum of propiolic acid (Figure 2) in cyclohexane shows absorption at 4.8 microns for the triple bond and at 5.9 microns for the carboxyl group. The results of an infrared spectrum (Figure 3) of the tetramethylammonium propiolate in n-butanol with a solvent

## IV Study of the Feasibility of Employing Acetylide Salts as Propellant Components, C (cont.)

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compensating cell shows absorption at 4.9 and 6.3 microns. The shift of the carboxyl group to a longer wave length when comparing an acid and its salt is described by Gilman (Reference 16).

5. In attempts to decarboxylate the propiolate, the compound was heated to its melting point (135°C) in an evacuated system and in the presence of nitrogen at one atmosphere. In both cases, a gas was evolved which mass spectrometer analysis showed to be acetylene. In the case of the evacuated system, as acetylene was evolved at the melting point, the liquid rapidly turned dark brown. After gas evolution was complete, the liquid resolidified at the same temperature, becoming progressively darker with time. Under nitrogen, a colorless liquid was produced at the melting point. After evolving gas, the liquid resolidified to a light, almost white solid. One portion of this solid was heated further, and at 210 to 225°C, began to darken slowly. At 260 to 265°C, the solid suddenly evolved a large quantity of gas and a fluffy carbonaceous residue resulted. Treatment of a second portion of the light, almost white solid described above with 6N HCl caused the vigorous evolution of a gas which was identified as CO<sub>2</sub>. Further attempts to decarboxylate this compound will be conducted at lower temperatures and in the presence of decarboxylation catalysts.

## D. REACTION OF TETRAMETHYLAMMONIUM TRIPHENYLMETHIDE WITH ACETYLENE

1. Attempts were made to prepare tetramethylammonium acetylide by the action of acetylene on tetramethylammonium triphenylmethide (Reference 4):



In carrying out this synthesis, extreme precautions were taken at all times to avoid contamination of the reaction mixtures with water, oxygen, or carbon dioxide, because each of these materials is known to be highly reactive toward, for example, the triphenylmethide anion. The various operations involved, such as filtration, were conducted precisely in the manner described by Schlenk (Reference 17). All materials were specially purified, and all gases were scrupulously freed of moisture, oxygen, and carbon dioxide.

2. The triphenylchloromethane (6.8 g) was allowed to react with 2% sodium amalgam (58 g) in ether (150 ml) to form sodium triphenylmethide. The solution was filtered under nitrogen in the manner described by Schlenk (Reference 17), and the clear, deep-red solution treated with tetramethylammonium chloride (13 g) until the chloride became coated with a red precipitate of tetramethylammonium triphenylmethide, with the simultaneous discoloration of the solution to light yellow. The precipitate was washed repeatedly with 30-ml portions of ether until the other washings were no longer yellow, and was then extracted with 100 ml of pyridine which had been

## IV Study of the Feasibility of Employing Acetylide Salts as Propellant Components, D (cont.)

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cooled to  $-30^{\circ}\text{C}$ . The resulting dark red solution was filtered under nitrogen, and acetylene was bubbled into the cold filtrate. Decoloration to light yellow occurred, and a very small amount of a white precipitate formed as the acetylene was absorbed.

3. The solid, after filtration and drying, did not melt at  $300^{\circ}\text{C}$ . It was found to be insoluble in water, acetic acid, benzene, ether, and dimethylformamide. However, it was soluble in concentrated hydrochloric acid, but without the liberation of gas. These observations indicate that the isolated solid could not have been tetramethylammonium acetylide. The pyridine filtrate was evaporated to dryness in vacuo, and the residual white solid was extracted with ether. Only partial solution occurred, and the insoluble portion was found to have the same properties as the high-melting material described above. The evaporation of the ether solution yielded a white solid, insoluble in water, mp  $90$  to  $91^{\circ}\text{C}$ . This is presumed to be triphenylmethane, lit. mp  $94^{\circ}\text{C}$ . Less than one gram of total solid material was isolated in these experiments, and it is evident that the extraction of tetramethylammonium triphenylmethide with pyridine is inefficient. Moreover, no indications of the formation of tetramethylammonium acetylide by the action of acetylene on tetramethylammonium triphenylmethide were obtained from the analytical procedures described above.

## E. DISCUSSION

1. During the course of this study of the feasibility of synthesizing non-metallic acetylide salts, consideration was given to the following diverse methods:

a. Reaction of tetramethylammonium salts with sodium acetylide in liquid ammonia and in organic solvents.

b. Reaction of tetramethylammonium free radical with acetylene in liquid ammonia.

c. Reaction of trimethylammonium methylid with acetylene.

d. Decarboxylation of tetramethylammonium propiolate.

e. Reaction of tetramethylammonium triphenylmethide with acetylene.

2. Although each of these methods embodies a different principle, no tetramethylammonium acetylide was isolated. Investigation of any one method may yet produce the desired salt, but such investigations would require further extensive effort, which appears to be unjustified in the light of present information. A final report on this phase of the program is in preparation.



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TABLE I

## THERMAL DECOMPOSITION OF NITROMETHANE

Product Analysis

Temperature: 355°C; Duration: 5 min

Product	$\frac{\text{moles product}}{\text{moles nitromethane decomp.}} \times 100$			
	Run 237	Run 238	Run 182	Average
CO <sub>2</sub>	19	19	20	19
CO	21	17	21	20
CH <sub>4</sub>	10	9	10	10
HCN	36	39	40	38
CH <sub>3</sub> CN	1	1	1	1
C <sub>2</sub> H <sub>5</sub> CN	3	3	1	2
CH <sub>2</sub> O	4	3	4	4
CH <sub>3</sub> OH	1	Trace	—	Trace
NO	53	53	54	53
N <sub>2</sub> O	—	3	4	3
N <sub>2</sub>	3	3	1	2
H <sub>2</sub> O	94	100	94	96

Table I



TABLE II

## THERMAL DECOMPOSITION OF NITROMETHANE

Per Cent Decomposition

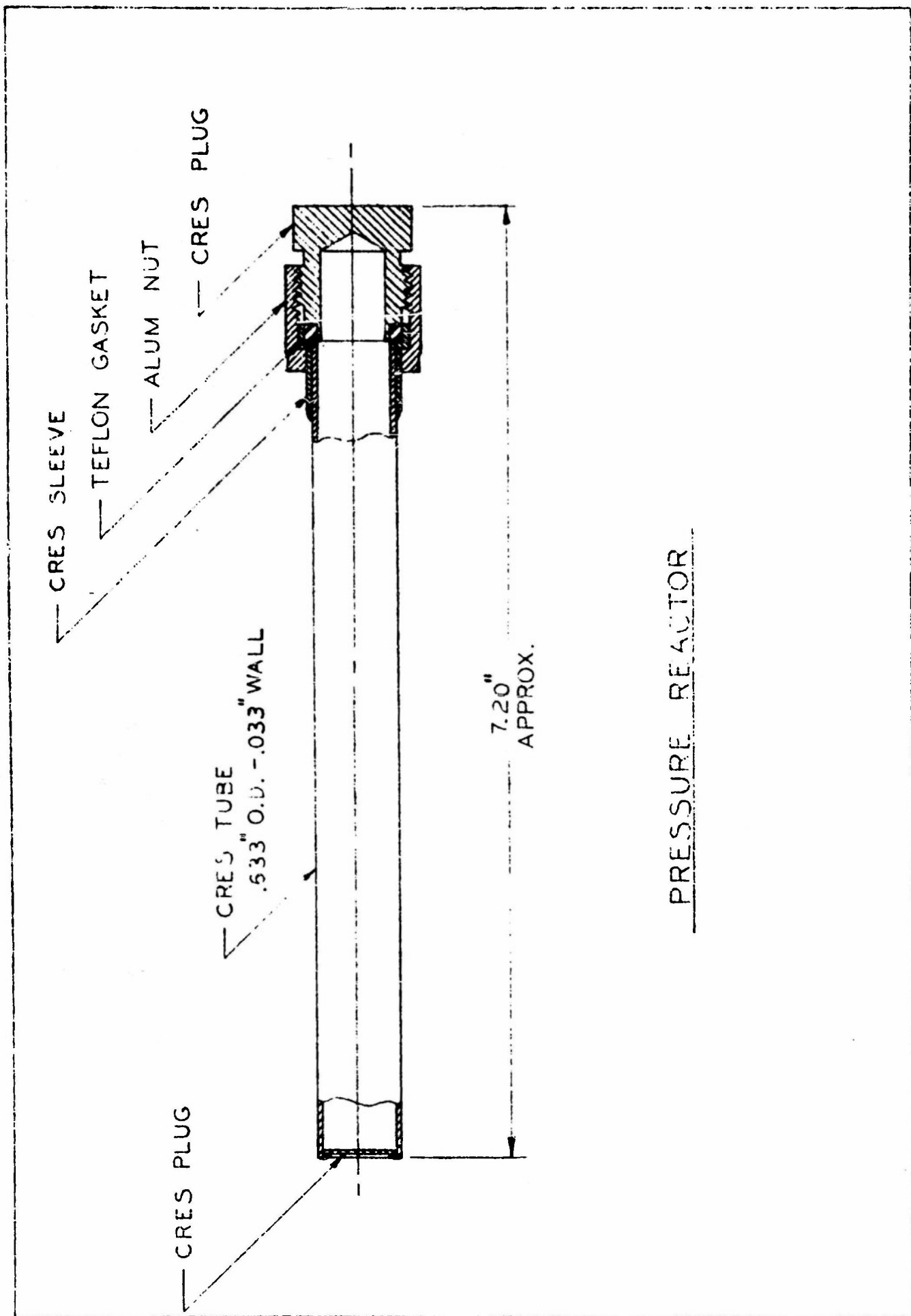
Temperature: 355°C, Duration: 5 min

Run No.	Additive	% Decomposition, Based on Total Carbon in Products	% Decomposition, Based on Total Nitrogen in Products	% Decomposition, Polarographic Analyses Mean and Std. Dev.*
237	None	5.9	5.7	5.1 $\pm$ 1.4
238	None	4.6	5.1	
182	None	6.4	7.0	
233	15.5 mole% oxygen	9.3	4.5	4.9 $\pm$ 2.7
245	15.4 mole% oxygen	9.1	2.6	
246	15.2 mole% oxygen	8.6	5.5	

\*

Reference 3

Table II



PRESSURE REACTOR

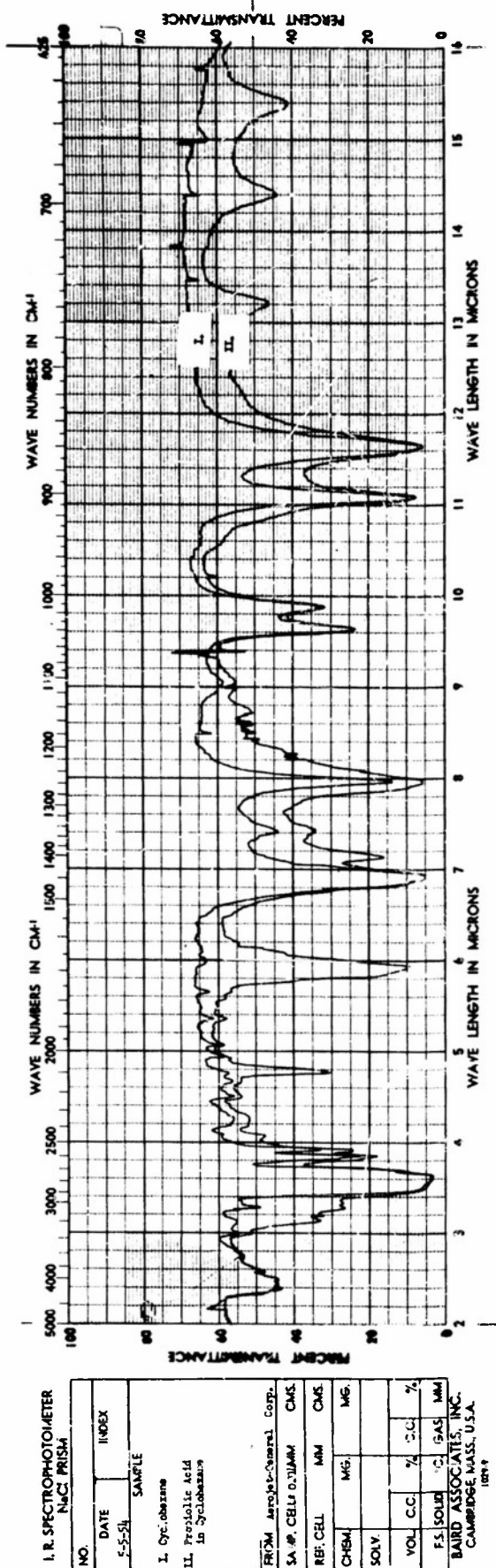


Fig. 2 Infrared Spectrum of Propionic Acid

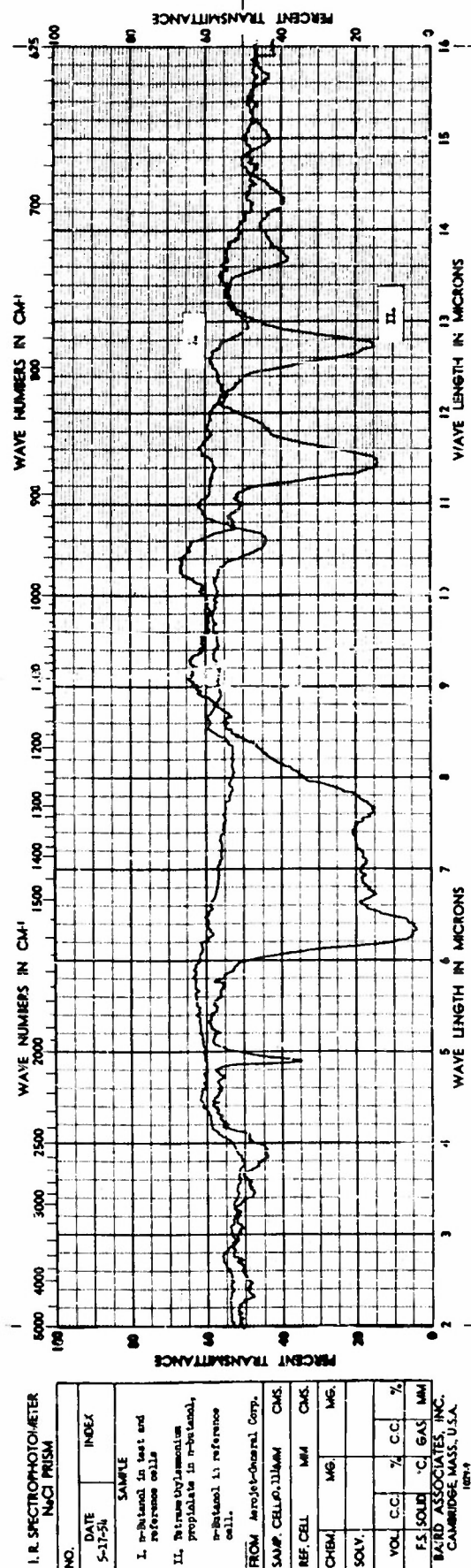


Fig. 3 Infrared Spectrum of Tetramethylammonium Propionate

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